



Modeling of conductivity relaxation in oxide ceramics taking account of concentration dependent chemical diffusivities and surface exchange coefficients

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ABSTRACT

Conductivity relaxation of disk-shaped ceramic samples upon a sudden change of the oxygen partial pressure of the surrounding gas phase has been simulated by application of a three-dimensional finite element model. The geometry is based on a homogeneous cylindrical specimen with a diameter of 10 mm and a thickness of 0.1 mm, where four peripheral line contacts are attached to the sample in accordance with the van der Pauw method. Both the chemical diffusion coefficient and the chemical surface exchange coefficient are assumed to vary with the oxygen non-stoichiometry during the oxygen exchange reaction (oxidation or reduction). The alteration of the oxygen non-stoichiometry as well as the relaxation of the electrical conductivity are calculated simultaneously. The modeling of conductivity relaxation curves is applied to the SOFC cathode material $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_{3-\delta}$ (LSF) at 900 °C. The simulation of conductivity relaxation curves can be performed for arbitrary oxygen partial pressure changes. The present modeling approach allows the interpretation of significant differences between oxidation and reduction steps owing to the concentration (non-stoichiometry) dependence of the kinetic parameters.

1. Introduction

Mixed ionically-electronically conducting solid oxides exhibit a certain deviation from the ideal stoichiometric composition, usually on the oxygen sublattice (oxygen non-stoichiometry), depending on temperature and oxygen partial pressure of the surrounding atmosphere. In general, the oxygen non-stoichiometry of mixed conducting ceramic oxides is accompanied with the simultaneous occurrence of electronic as well as ionic point defects, such as holes and oxygen vacancies. The change of the oxygen activity in the ambient gas phase gives rise to the alteration of the oxygen non-stoichiometry. The kinetics of this oxygen exchange reaction is decisive for the polarization resistance of SOFC (solid oxide fuel cell) cathode materials [1,2]. Moreover, the rate of re-oxidation processes of electroceramics is governed by oxygen exchange reactions [3]. The kinetics of the oxygen exchange reaction between the gas phase and the solid phase is determined by the surface exchange reaction and chemical diffusion of oxygen through the ceramic sample [4,5].

Conductivity relaxation experiments are a powerful technique for the determination of the relevant kinetic parameters (chemical diffusion coefficient and chemical surface exchange coefficient) [6–10]. In addition, numerical simulations of conductivity relaxation curves

caused by oxygen exchange have become an inevitable tool for a better insight into transport processes of oxide ceramics [11–15]. Moreover, statistical analyses have been carried out in order to improve the accuracy for the determination of chemical diffusion coefficients and surface exchange coefficients from conductivity relaxation curves [16–18].

It is the aim of this work to introduce a finite element model which enables numerical simulations of the relaxation of the electronic conductivity due to an instantaneous change of the oxygen activity of the gas phase surrounding a disk-shaped ceramic sample. The van der Pauw method is used for the determination of the electronic conductivity of the mixed conducting oxide with predominant electronic conduction, i.e. the electronic transport number is close to unity. In particular, the present modeling approach is applied to calculate conductivity relaxation curves for arbitrary steps of the oxygen partial pressure by taking account of the concentration (oxygen non-stoichiometry) dependence of the chemical diffusivity as well as the surface exchange coefficient. The simulations, representing an extension of the linear response (small signal behavior) to large variations of the activity of the mobile neutral component (oxygen) with respect to both the chemical diffusion process and the surface exchange reaction, are applied to $\text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_{3-\delta}$ at 900 °C which is a typical model material for SOFC

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cathodes. The numerical modeling of conductivity relaxation curves is suitable for the interpretation of significant differences between oxidation and reduction runs which have frequently been reported in literature [7,10,19,20].

2. Theoretical aspects

The alteration of the oxygen partial pressure, $p(\text{O}_2)$, of the gas phase surrounding a mixed electronically-ionically conducting oxide ceramic sample in a step-wise manner leads to oxidation/reduction (oxygen exchange reaction) of the solid specimen. The incorporation/release of oxygen into/from the solid oxide results in a variation of the oxygen non-stoichiometry with time. This change of the non-stoichiometry is related to a variation of the electronic conductivity which can be detected, e.g., by means of the van der Pauw method. Hence, a proper analysis of the relaxation of the electronic conductivity upon a sudden change of the oxygen activity yields the chemical diffusion coefficient and the chemical surface exchange coefficient which are decisive for the phenomenological description of the chemical diffusion process and the rate of the surface reaction. Usually, the oxygen partial pressure steps are kept sufficiently small [$\Delta \ln p(\text{O}_2) \ll 2/z_{\text{O}}$ with z_{O} being the number of oxygen atoms involved in the rate-determining step], such that the linear response of the solid sample to a small signal (perturbation from equilibrium) is analysed by fitting analytical solutions of the diffusion equations to experimental data (conductivity relaxation curves). A necessary requirement for this technique is the invariance of the phenomenological parameters (chemical diffusion coefficient and surface exchange coefficient) with the oxygen non-stoichiometry during the conductivity relaxation experiment, i.e. the chemical diffusion coefficient is assumed to be spatially invariant and the surface exchange coefficient may not vary with oxygen partial pressure and/or oxygen non-stoichiometry of the sample. These constraints are only fulfilled for fairly small alterations of the oxygen activity of the gas phase which might result in difficulties regarding the experimental determination of small conductivity changes as a function of time. Basically, both the chemical diffusion coefficient and the surface exchange coefficient are known to depend on the oxygen partial pressure/oxygen non-stoichiometry. Especially in the case of relevant cathode materials, such as LSF [10], the surface exchange coefficient increases strongly with increasing $p(\text{O}_2)$, while the electronic conductivity shows a fairly smooth variation with the oxygen partial pressure [21]. Hence, experimental conductivity relaxation curves might deviate remarkably from the analytical solution functions of the diffusion equations because too large $p(\text{O}_2)$ – steps (exceeding the linear response regime) might be required for experimental reasons.

A three-dimensional finite element model has been developed in order to simulate conductivity relaxation curves for arbitrary oxygen partial pressure steps, i.e. the dependence of the chemical diffusion coefficient and chemical surface exchange coefficient on the diffusant concentration, c , and oxygen partial pressure has been taken into account. The numerical calculations are applied to a disk-shaped sample with a thickness $L = 0.1$ cm and a diameter $2 r_0 = 1.0$ cm. The transport of oxygen (neutral mobile component) through the ceramic sample, e.g. via oxygen vacancies and holes, can be expressed as

$$\frac{\partial c}{\partial t} = \text{div}(\tilde{D} \text{grad } c) \quad (1)$$

which is a linear partial differential equation (Fick's second law) only in the case of constant (spatially invariant) chemical diffusivities \tilde{D} . The concentration dependence of \tilde{D} is given by the vacancy diffusion coefficient, D_{V} , and the thermodynamic factor, ϑ_{V} ,

$$\tilde{D} = D_{\text{V}} \vartheta_{\text{V}}; \vartheta_{\text{V}} = -\frac{1/2 \text{d} \ln p(\text{O}_2)}{\text{d} \ln \delta} \quad (2)$$

with δ being the oxygen non-stoichiometry and $c = (3 - \delta) / V_{\text{m}}$ ($\text{d}c = -\text{d}\delta / V_{\text{m}}$, where V_{m} denotes the molar volume). Usually, the

vacancy diffusivity is almost independent of the non-stoichiometry, whereas the thermodynamic factor is a distinct function of the oxygen non-stoichiometry which is given by the defect chemistry of the material and can be calculated by means of a proper thermodynamic model. The boundary condition for the surface exchange reaction can be written as

$$J_{\text{O}} = -\tilde{D} \frac{\partial c}{\partial n} = -\tilde{k} (c - c_{\infty}), \quad (3)$$

where \tilde{k} , $\partial/\partial n$, and c_{∞} denote the chemical surface exchange coefficient, differentiation along the normal of the surface, and the diffusant (oxygen) concentration after re-equilibration (end of relaxation process, $t \rightarrow \infty$), respectively [22,23]. Eq. (3) is non-linear, if the kinetic parameter is a function of oxygen partial pressure and/or non-stoichiometry. The surface exchange coefficient is related to $p(\text{O}_2)$ and δ by

$$\tilde{k} = a p(\text{O}_2)_{\text{final}} \delta^m \frac{\vartheta}{(3 - \delta)}; \vartheta = \frac{1/2 \text{d} \ln p(\text{O}_2)}{\text{d} \ln c} \quad (4)$$

The symbol a includes, besides the molar volume, the rate constant for the forward reaction of the rate-determining step as well as equilibrium constants for pre-equilibria of fast preceding reaction steps. A detailed derivation of Eq. (4) can be found in Appendix A. Basically, the chemical surface exchange coefficient is a function of the thermodynamic factor, the final oxygen partial pressure at the end of the relaxation process assuming that molecular oxygen (two oxygen atoms) is involved in the rate-determining step, and the oxygen non-stoichiometry with a formal reaction order m . As the oxygen partial pressure is changed instantaneously, its final value is attained immediately, such that $p(\text{O}_2) = p(\text{O}_2)_{\text{final}}$ is constant throughout the relaxation process. On the contrary, the oxygen non-stoichiometry as well as the thermodynamic factor will change gradually during the relaxation process. It is worth mentioning that besides oxygen vacancies also electronic charge carriers can be involved in the rate-determining step or in pre-equilibria of fast preceding reaction steps. Since the concentration of electronic charge carriers depends on the oxygen non-stoichiometry, a gradual change can likewise be expected during the relaxation process. Thus, the relationship between the surface exchange coefficient and electronic charge carriers as well as oxygen vacancies is given by δ^m .

The determination of the electronic conductivity is facilitated by the van der Pauw technique. Four peripheral equidistant line contacts are employed for this purpose. Two serve as current carrying electrodes, while the opposite two contacts are the voltage probes. A high electronic conductivity is taken for the line contacts $\sigma_{\text{contact}} = 1000 \text{ S cm}^{-1}$ with zero diffusivity. A constant current of $I = 0.10 \text{ A}$ is applied to the electrodes. Assuming predominant electronic conduction in the mixed conducting oxide ($t_{\text{e}} \approx 1$), the current density reads

$$j = \frac{\sigma_{\text{e}}}{F} \text{grad } \tilde{\mu}_{\text{e}} \quad (5)$$

with σ_{e} and F being the electronic conductivity and Faraday constant, respectively. The gradient of the electrochemical potential of electrons is related to the electrical potential gradient (consistent with the externally applied electric field necessary for the determination of the electronic conductivity), $\text{grad } \tilde{\mu}_{\text{e}} \approx -F \text{grad } \phi$, as polarization processes at the electrodes are neglected, i.e. concentration gradients may be exclusively caused by the oxygen exchange reaction. Furthermore, any interfacial resistances between the ceramic sample and the electronic contacts (e.g. Pt – or Au – electrodes) are disregarded. The continuity equation for charge transport is defined as

$$\text{div } j = 0, \quad (6)$$

where the current density is given by Eq. (5) and the electronic conductivity, which is a function of time and space, is coupled with the oxygen non-stoichiometry [non-linear coupling in the case of large $p(\text{O}_2)$ – steps]. In accordance with the van der Pauw technique the boundary condition for one current carrying contact is given by

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